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SYNTHESIS AND BALLISTIC EVALUATION OF SELECTED
TRANSPARENT POLYURETHANE BLOCK COPOLYMERS,
PART II. FURTHER CHANGES IN FORMULATION

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POLYMER AND CHEMISTRY DIVISION

March 1975

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ABSTRACT

In an extension of previous work on polyurethane block copolymers for transparent armor applications, several additional variations of the basic 2,4-toluene diisocyanate/polytetramethylene oxide/1,4-butanediol formulation have been investigated. It has been found that excess diisocyanate in a given formulation improves ballistic resistance and that decreasing the amount of polyether (soft segment) has the same effect. The material with the lowest soft segment content yet tested shows a dramatic improvement in V_{50} over earlier specimens. More generally, it has been found that increased sample hardness (Shore D) parallels improved ballistic performance. High-speed photographic data have shown that these materials continue to absorb large amounts of ballistic energy above the V_{50} values, with relatively little of this energy manifested as fragment kinetic energy. A technique for the preparation of void-free ballistic test specimens involving the use of a polytetrafluoroethylene mold is also described. (Authors)

CONTENTS

INTRODUCTION

In previous reports[1,2] we have described our initial investigation of poly-
urethane block copolymers as potential transparent armor materials. In that work
the effect was studied of several variations in formulation and processing on the
V_{50} ballistic performance[2] of polyurethane block copolymers prepared from 2,4-
toluene diisocyanate (TDI), polytetramethylene oxide (PTMO), and 1,4-butanediol
(BD). These variations included cure time, cure temperature, polyether molecular
weight, TDI and BD content, and the presence of an inhibitor (benzoyl chloride)
to control void formation. The best material had a V_{50} of 955 fps at an areal
density of 22 oz/sq ft.

In this present study, further variations in processing and formulation of
the basic TDI/PTMO/BD copolymer have been investigated. An improved method for
the preparation of void-free ballistic samples has been developed which, when
used in conjunction with an improved formulation, has led to a dramatic increase
in ballistic performance. This material has a V_{50} of 1062 fps which is within
2% of that of the best lightweight bulk transparent armor material yet developed.
Specifics of the variations and their effect on ballistic performance are dis-
cussed in detail below.

EXPERIMENTAL

Polymer Synthesis

The polymers studied in this work were prepared in exactly the same manner
as described previously.[1] Figure 1 depicts the idealized chemical structure of
this polyurethane block copolymer.

Specimen Preparation

The casting syrup obtained from the synthesis was poured into a 6" × 6" × 1/4"
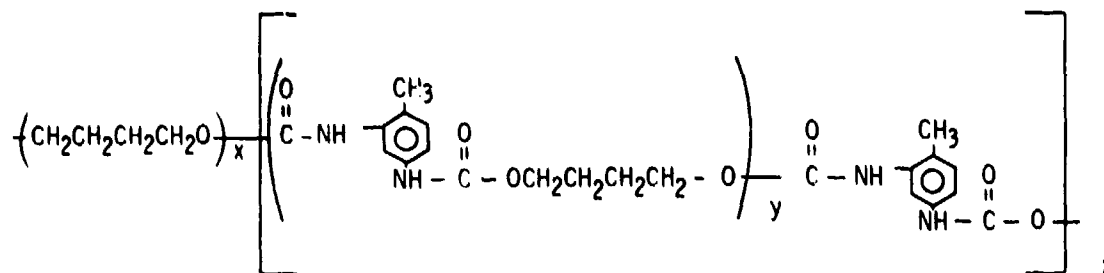cavity which had been milled into a 1/2" sheet of polytetrafluoroethylene. It was

Figure 1. Idealized structure of PTMO/2,4-TDI/BD polyurethane block copolymer.

1. WILDE, A. F., MATTON, R. W., ROGERS, J. M., and WENTWORTH, S. E. *Synthesis and Ballistic Evaluation of Selected Trans-
   parent Polyurethane Block Copolymers.* Army Materials and Mechanics Research Center, AMMRC TR 73-53, December 1973.
2. WILDE, A. F., MATTON, R. W., ROGERS, J. M., and WENTWORTH, S. E. *The Preparation and Ballistic Evaluation of Transparent
   Polyurethane Block Copolymers Based on 2,4-Toluene Diisocyanate.* Proceedings of the 1974 Army Science Conference, U. S.
   Military Academy, West Point, N. Y., v. 3, June 1974, p. 315-29.

found that treatment of this mold with a very light film of silicone oil and pre-heating to 100 C aided in the production of void-free specimens. The filled mold was placed in an oven and cured overnight at 100 C. The cured polymer sheets were wrapped in polyethylene and stored under ambient conditions until tested.

Hardness Measurements

The hardness of each specimen was determined by use of a hardness tester: Shore Durometer, Type D.

Ballistic Testing and High-Speed Photography

The ballistic performances were determined and high-speed photographs were taken in the manner described previously.[1,2] The ballistic performances were expressed in terms of the V_{50} value which is the average velocity at which the specimen is or is not just barely penetrated completely by the projectile. The ballistic impacts were made with the standard .22 cal. fragment simulator projectile (FSP).

RESULTS AND DISCUSSION

Effect of Diisocyanate/Diol Mole Ratio

Because of the projected use of there materials in transparent armor applications, it is desirable to have as little color as possible. Our specimens formulated with TDI, PTMO, and BD have been pale brown or pale yellow in color. It is believed that a principal cause of this color is the presence of excess isocyanate. Up to this point, our specimens had been deliberately formulated with a diisocyanate/diol mole ratio of 1.05 in order to control molecular weight.

We then systematically reduced the diisocyanate/diol mole ratio from 1.05 to 0.95, as shown in Table 1, but, unfortunately, there was no concurrent reduction

Table 1. FORMULATION AND PROPERTIES OF SPECIMENS WITH VARIATIONS IN DIISOCYANATE/DIOL MOLE RATIO

Specimen	Composition in Mole Ratios		Diisocyanate/Diol Mole Ratio	Shore D Hardness	V_{50}* and Spread fps
1011-195	TDI	5.25	1.05	40-45	V_{50} = 969
	PTMO 1070	1.00			Spread = 42
	BD	4.00			
1011-196	TDI	5.00	1.00	34-39	V_{50} = 906
	PTMO 1070	1.00			Spread = 68
	BD	4.00			
1011-197	TDI	5.00	0.95	19-24	V_{50} = 830
	PTMO 1070	1.05			Spread = 66
	BD	4.20			

*V_{50} normalized to 22.0 oz/sq ft areal density, based on 8-shot tests.

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in degree of coloration of the specimens. Surprisingly, however, this small change in stoichiometry produced significant effects both in specimen hardness and in ballistic performance. These effects are illustrated graphically in Figure 2. Both the V_{50} and the Shore D hardness decreased considerably with the decrease in the diisocyanate/diol mole ratio; the lowest ratio specimen was so soft that it sagged under its own weight when not fully supported. We have speculated that the higher ratios of the diisocyanate may increase the small amount of crosslinking that probably occurs and/or may change the nature of the interaction between the soft and hard domains in the final block copolymer. In any event, at this time there appears to be no advantage in using the lower diisocyanate/diol mole ratios.

All of the specimens in this series exhibited a completely ductile response to ballistic impact, producing no spall or radial cracking, and generating just a small shear plug plus a few very fine particles.

Effect of Soft Segment/Hard Segment Ratio

Our previous investigations[1,2] had indicated that the ballistic performance of these materials was improved by increasing the hardness or rigidity of the specimens if we could simultaneously retain their ductile failure characteristics. In the present work we undertook to extend this concept by further reductions in the soft segment content. The formulations and properties of this series are shown in Table 2 where the soft segment content was reduced from 45.7 to 33.9
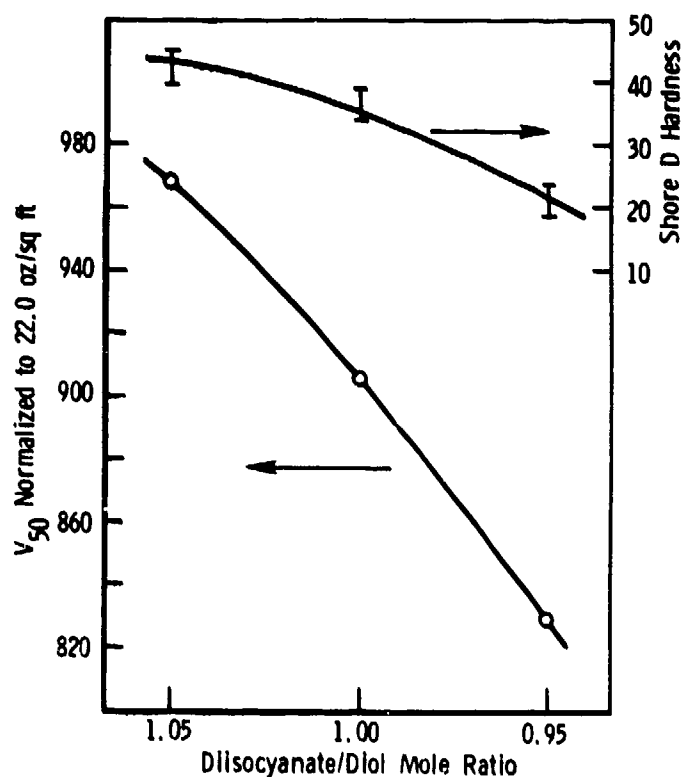
Figure 2. Specimen hardness and ballistic performance as functions of diisocyanate/diol mole ratio.

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weight percent. All of the specimens in this series also responded in a completely ductile fashion to the ballistic impacts, except for the lowest soft-segment material where some incipient radial cracking was just barely in evidence.

The graphical results for this series appear in Figure 3. Both the V_{50} and the Shore D hardness increased monotonically with the decrease in soft segment content. This agreed with the trend noted in our previous work[1,2] and extended the ballistic performance to the highest value we have yet attained with a transparent polymeric material synthesized in-house.

These results can be compared with the ballistic performances (Table 3) of the two outstanding commercial ductile transparent polymers which we use as benchmarks. The polycarbonate offers the best combination of properties in commercial materials in terms of ballistic performance, optical clarity, and commercial availability. The developmental commercial polyurethane presently exhibits the highest ballistic performance of any transparent polymer but is handicapped by a dark yellow color and by nonavailability due to the toxicity of one of its components. It is seen that our best formulation has a V_{50} within 2% of this latter commercial material and hence offers promise as an outstanding candidate for transparent armor application.

Table 2. FORMULATION AND PROPERTIES OF SPECIMENS WITH
VARIATIONS IN SOFT SEGMENT/HARD SEGMENT RATIO

Specimen	Composition in Mole Ratios		Weight Percent Hard	Soft	Shore D Hardness	V_{50}* and Spread fps
1011-195	TDI	5.25	54.3	45.7	40-45	V_{50} = 969
	PTMO 1070	1.00				Spread = 42
	BD	4.00				
1187-15B	TDI	6.30	59.1	40.9	52-57	V_{50} = 1014
	PTMO 1070	1.00				Spread = 56
	BD	5.00				
1011-199	TDI	7.35	63.0	37.0	63-68	V_{50} = 1057
	PTMO 1070	1.00				Spread = 50
	BD	6.00				
1011-200	TDI	8.40	66.1	33.9	71-76	V_{50} = 1062
	PTMO 1070	1.00				Spread = 34
	BD	7.00				

*V_{50} normalized to 22.0 oz/sq ft areal density, based on 8-shot test.

Table 3. BALLISTIC PERFORMANCE OF COMMERCIAL
TRANSPARENT POLYMERS

Polymer	V_{50} (fps) Normalized to 22.0 oz/sq ft
Commercial polycarbonate	850
Developmental commercial polyurethane	1080

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Figure 3. Specimen hardness and ballistic performance as functions of soft segment content.
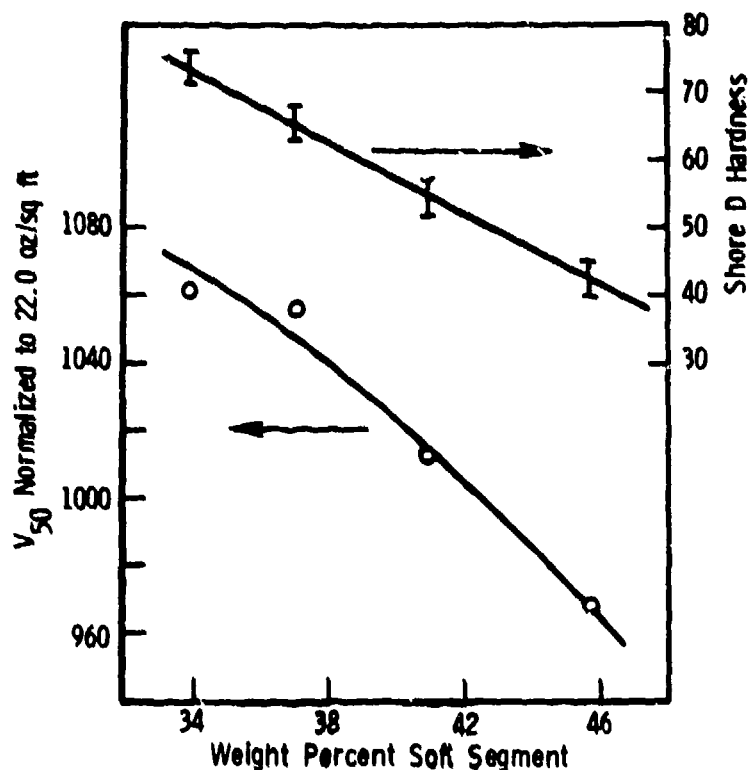
Development of a Void-Free Casting Technique

In our previous work[1] a good deal of effort was devoted to the elimination of voids from the ballistic test specimens. The problem was particularly severe with samples cured at elevated temperatures. Since a 100 C cure resulted in specimens with superior ballistic performance (in spite of voids), it was especially important that this problem be solved.

Such a solution has been found in the simple replacement of the RTV silicone test specimen mold with one made of polytetrafluoroethylene (see Experimental). It has been found necessary to surface treat the mold with an extremely light film of silicone oil and to preheat it to 100 C prior to casting. Using this technique, it has been possible to obtain nearly void-free specimens even after a 100 C overnight cure. Because of a tendency of the mold to curl slightly on heating, resulting in specimens of nonuniform thickness, we have resorted to bolting it to a 1/4"-thick sheet of steel (see Figure 4). This has the added advantage of maintaining the elevated temperature of the preheated mold during the casting operation which can thus be done under ambient conditions rather than in an oven.

General Relationship Between Hardness and Ballistic Performance

From the data presented in Figures 2 and 3 it is evident that the ballistic performance and the hardness of these materials are both affected in a similar fashion by changes in copolymer formulation. To illustrate this relationship more

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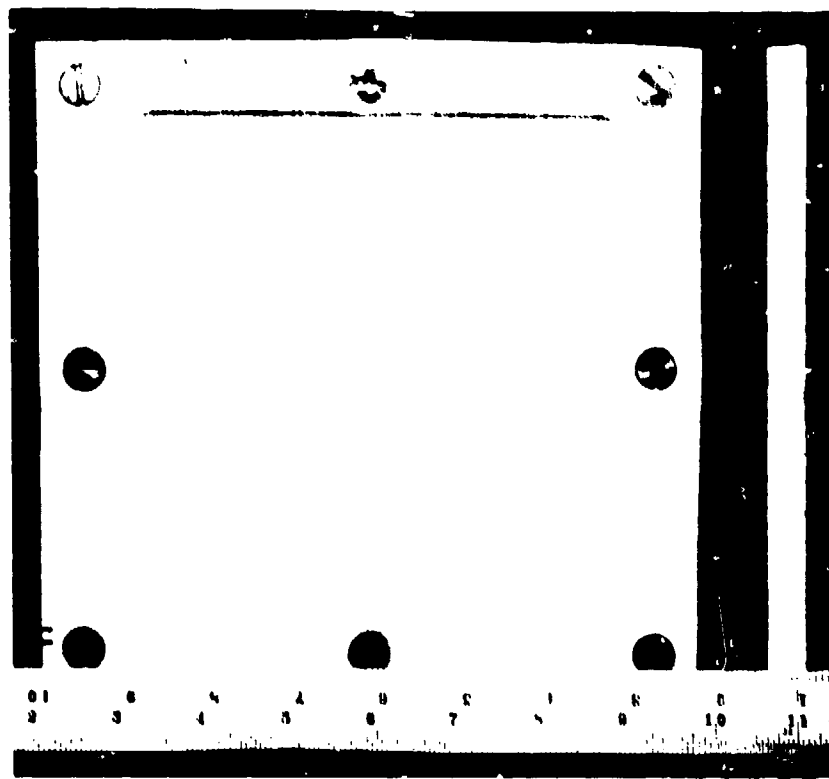
Figure 4. Polytetrafluoroethylene mold.
Polytetrafluoroethylene mold bolted to
steel plate. Top view and edge view.
Scale in inches.
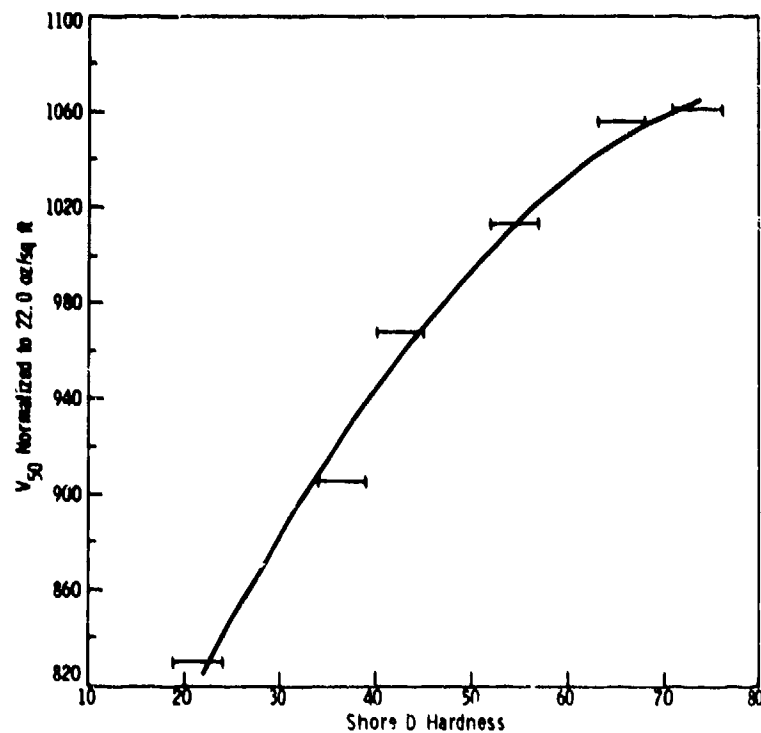
Figure 5. Ballistic performance as a function
of specimen hardness for 2,4-TDI/PTMO/BD
block copolymers displaying ductile failure
characteristics.

clearly, the ballistic performance was plotted against the hardness as in Figure 5. It is seen that there is a monotonic trend between the two, the softer specimens having the lower V_{50} values.

This type of relationship has been noted previously in this laboratory with polymers which undergo ductile response to ballistic impact. For example, polycarbonate was block copolymerized with various amounts of polydimethylsiloxane, a silicone rubber.[3] The V_{50} values dropped monotonically with increasing silicone rubber content. An explanation was made as follows. As long as the predominant response is ductile, the failure occurs by a plastic deformation process. The impact resistance of such a material may well depend upon its yield strength because this affects the energy absorbed during plastic deformation. Addition of further rubber (or soft-segment material) would simply lower the yield strength without changing the deformation mechanisms and thus would only decrease the ballistic performance.

Another example is given by a series of rubber-modified polymers where a normally brittle matrix polymer is blended with grafted rubber particles.[4] Beyond a certain critical rubber content, the system becomes predominantly ductile in its response to ballistic impact, and further addition of rubber causes a decrease in the ballistic performance. A similar explanation based on reduced yield strength might also apply here.

In the present work, as exemplified in Figure 5, we assume that hardness can be considered as an inverse measure of the rubbery nature or the rubber content of these specimens. Our variations in this rubbery behavior had been achieved either by changing the diisocyanate/diol mole ratio or by changing the soft segment/hard segment ratio. The softer specimens (more rubbery behavior) exhibited lower ballistic performance, in agreement with the two examples cited above. Hence, for this class of polyurethane block copolymers displaying ductile failure characteristics, the influence of specimen hardness upon V_{50} is probably a manifestation of similar relationships between rubbery behavior, yield strength, and energy absorption.

High-Speed Photographic Investigation of Ballistic Impact

Figure 6 is a typical multiple-exposure high-speed photograph which depicts both the FSP and the specimen plug (plus a few very fine particles) just after penetration of the specimen. The photographs were taken at striking velocities (V_S) which ranged from about the V_{50} value up to approximately 200 m/sec (656 fps) higher. The photographs permit calculation of the FSP residual velocity (V_R) and the velocity of fragments or plugs (V_F) generated from the polymer specimen by the impact.

The experimentally determined values of V_R and V_F are plotted in Figure 7 as a function of the normalized FSP striking velocity for the four specimens

3. ROYLANCE, M. E., and LEWIS, R. W. *Development of Transparent Polymers for Armor.* Army Materials and Mechanics Research Center, AMMRC TR 72-23, July 1972.
4. BAUM, B., STISKIN, H., and WILDE, A. F. *Transparent, Impact-Resistant, Rubber-Modified Acrylic.* Presented at symposium on Toughness and Brittleness of Plastics, American Chemical Society National Meeting, Atlantic City, N. J., September 1974; to be published by the A.C.S. in its Advances in Chemistry series.
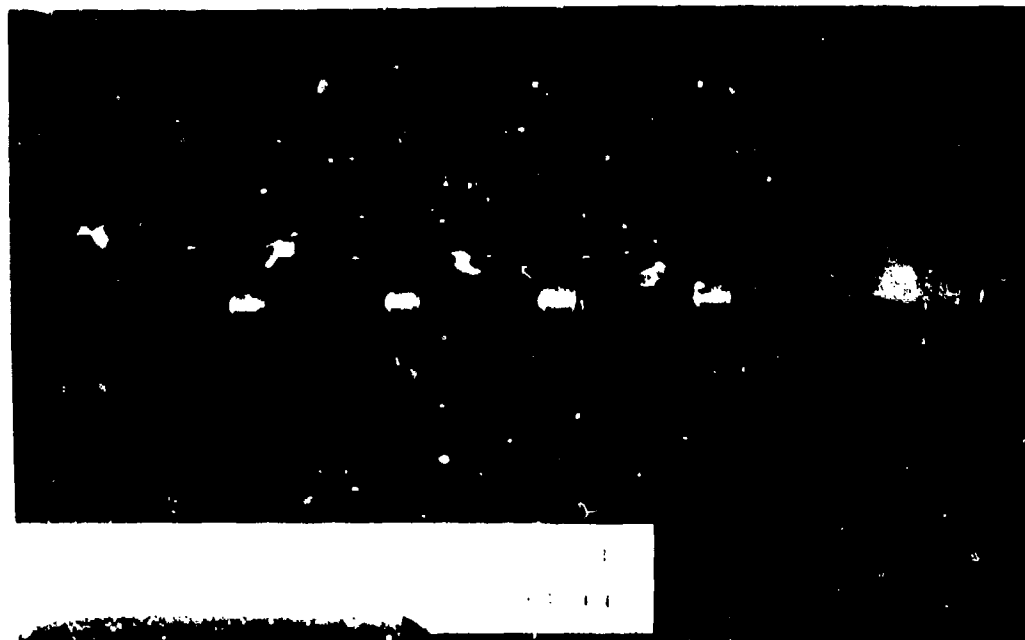
Figure 6. Ductile penetration of polyurethane specimen. High-speed photograph just after FSP penetration from right to left. Five flashes. 100 μsec between flashes. V_S = 397 m/sec, V_R = 267 m/sec, V_F = 317 m/sec. Scale in centimeters.
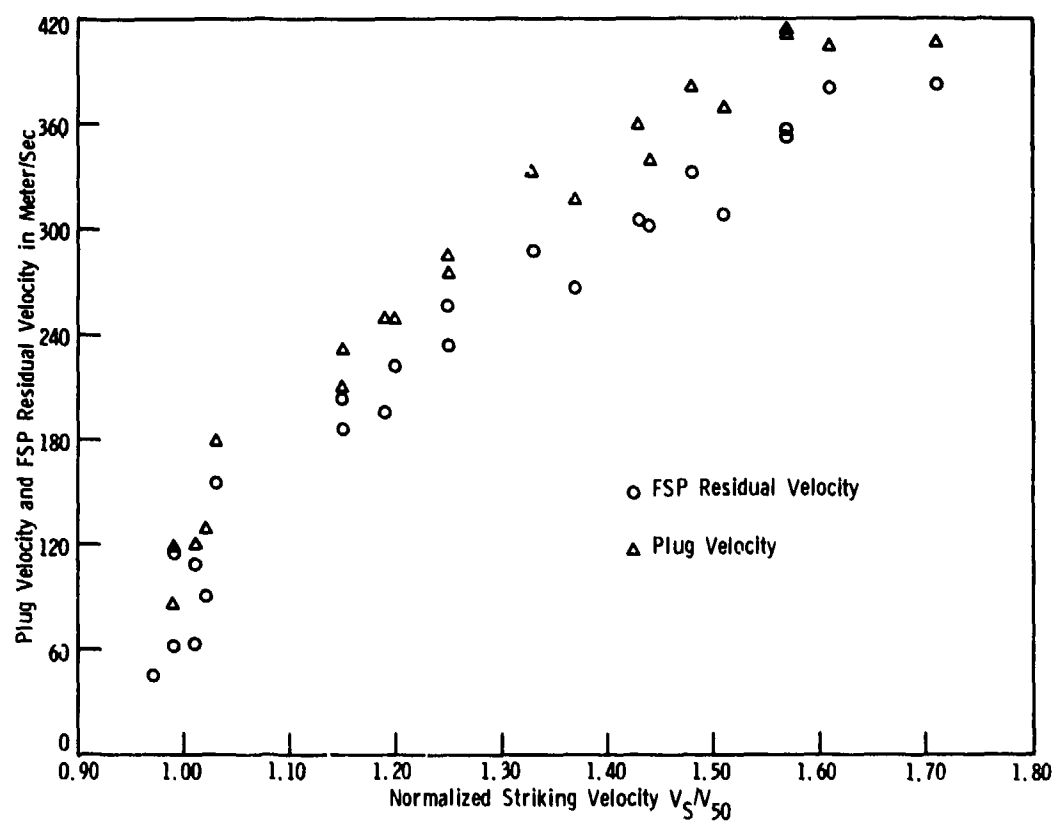

Figure 7. Plug velocity and FSP residual velocity as functions of the normalized striking velocity for four polyurethane copolymer specimens.

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listed in Table 2. (Because data for catastrophic events such as impact, fracture, and fragmentation are inherently subject to scatter, clear trends in the results become evident only for a large number of data points; hence the data for all four specimens were combined. Because these specimens used here cover a range of V_{50} values, the striking velocities for each specimen were normalized to the V_{50} value for that specimen.) The plot shows that both V_R and V_F increase quite rapidly with V_S in the vicinity of V_{50} and that the rate of increase becomes less at the higher values of V_S. It is also evident that V_F generally exceeds V_R at a given V_S. These results extend the range of striking velocities over that investigated and reported previously for polyurethane materials.[1]

Velocity data of this sort can be used to determine the approximate FSP energy loss, ΔE, occurring during penetration of the polymer specimen. When V_S exceeds the V_{50}

$$\Delta E = 1/2 \ M \ (V_S^2 - V_R^2) \tag{1}$$

where M is the mass of the FSP. These energy losses are plotted in Figure 8 in normalized form to allow presentation in one graph of the results for all four specimens. When V_S is less than the V_{50}, $V_R = 0$, and

$$\Delta E = 1/2 \ M \ V_S^2 \tag{2}$$
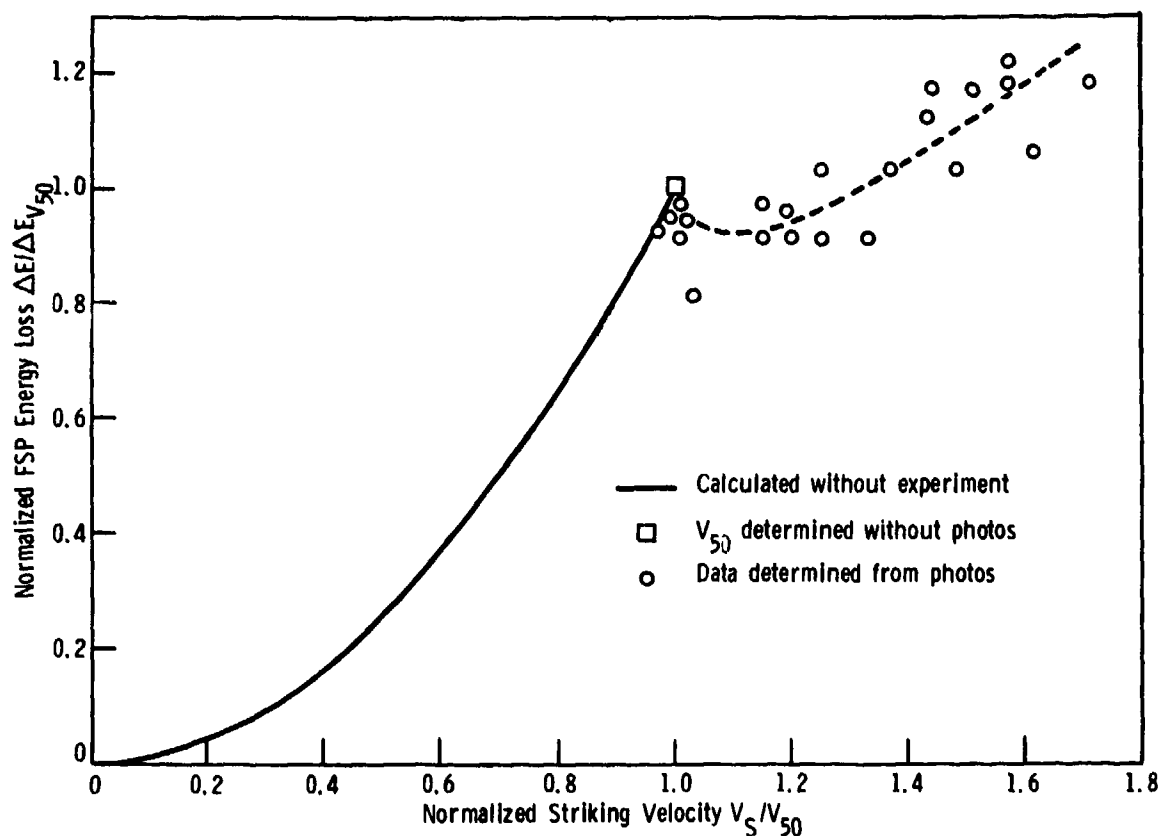
Figure 8. Normalized FSP energy loss as a function of normalized striking velocity.

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from which the curve can be drawn directly without experiment, and is shown by the solid line in Figure 8. It is seen that immediately above the V_{50} value ΔE decreases slightly; at higher V_S values ΔE increases, but at a rate considerably less than that below the V_{50}. These energy loss results indicate that these ductile polyurethane block copolymers continue to absorb large amounts of projectile kinetic energy as V_S increases above the V_{50} value, unlike the behavior of textile materials, but generally similar to the behavior of metals and brittle polymers.[5]

These same data points can be used to determine the fraction of the FSP initial kinetic energy lost during the penetration process. Such a plot is shown in Figure 9 as a function of the normalized striking velocity. Above the V_{50} value this fraction drops monotonically from 1.0 despite the increase in the absolute energy loss. This occurs because the FSP initial kinetic energy is increasing more rapidly with V_S than is the energy loss, hence the ratio of the two decreases. This behavior appears to be typical for most armor materials above the V_{50}.

The plug velocity data in Figure 7 were used to furnish an estimate of the kinetic energies contained in the specimen fragments after penetration. The average plug mass was about 0.06 gram; this led to approximate plug kinetic energies ranging from 1 to 5 joules. These values comprised from about 2 to 9% of the corresponding FSP energy losses, where the higher percentages occurred at the higher striking velocities. Hence, it is apparent that the plug kinetic energies constitute only a minor fraction of the total FSP energy losses with these ductile polyurethane block copolymers in specimen thicknesses of about 1/4 inch. The major component of the FSP energy loss is presumably expended in plastic deformation of specimen and plug and in creation of fracture surfaces on these bodies.
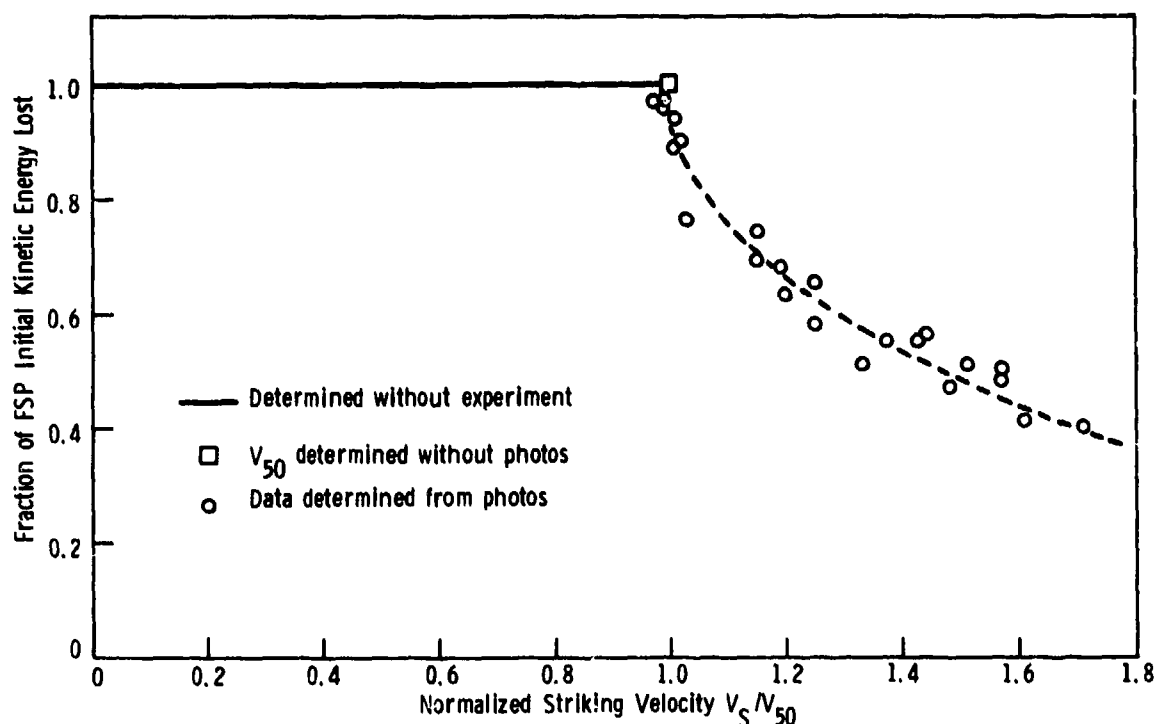
Figure 9. Fraction of FSP initial kinetic energy lost during interaction with polymer specimen as a function of normalized striking velocity.

5. ALESI, A. L. *Composite Personnel Armor.* Quartermaster Research and Engineering Center, Natick, Ma., Technical Report CP-5, December 1957. (Confidential Report)

SUMMARY AND CONCLUSIONS

The AMMRC polyurethane block copolymers have now shown the following characteristics:

1. high V_{50} values which can nearly match the best transparent polymeric material;

2. ductile response to ballistic impact; this eliminates catastrophic failure, minimizes the production of dangerous secondary fragments, and preserves optical integrity; and

3. high degree of transparency.

With these ductile materials, the relationship between hardness and ballistic performance appears similar to that for other ductile polymers. Analysis of the high-speed photographs has indicated that these polyurethane materials continue to absorb large amounts of FSP kinetic energy at striking velocities well above the V_{50} value and that the plug kinetic energies comprise only a minor fraction of this energy loss.

It is concluded that additional improvements in the ballistic performance of these polyurethane block copolymers might be achieved by further increases in the specimen hardness (probably to the point where brittle response to impact becomes the predominating mode of failure). Among the routes available for this expected ballistic improvement is the approach involving further reduction in the soft-segment content.

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